can now be considered secure from railway injury, he wishes to make them public, in hopes that they may be useful, not only to practical astronomy, but to some other departments of science.

V. "Preliminary Notice of an Examination of *Rubia munjista*, the East-Indian Madder, or Munjeet of Commerce." By JOHN STENHOUSE, LL.D., F.R.S. Received June 18, 1863.

It is rather remarkable that while few vegetable substances have been so frequently and carefully examined by some of the most eminent chemists than the root of the *Rubia tinctorum*, or ordinary madder, the *Rubia munjista*, or munjeet, which is so extensively cultivated in India and employed as a dye-stuff, has been, comparatively speaking, very much overlooked, never having been subjected, apparently, to anything but a very cursory examination. Professor Runge, at the close of his very elaborate memoir upon madder, published in 1835, details a few experiments which he made upon the tinctorial power of munjeet, the constituents of which he regarded as very similar to those of ordinary madder. Professor Runge stated that munjeet contains twice as much available colouring matter as the best Avignon madder. This result was so unexpected that the Prussian Society for the Encouragement of Manufactures, to whom Professor Runge's memoir was originally addressed, referred the matter to three eminent German dyers, Messrs. Dannenberger, Böhm, and Nobiling. These gentlemen reported, as the result of numerous carefully conducted experiments, that, so far from munjeet being richer in colouring matter than ordinary madder, it contained only half the quantity. This conclusion has been abundantly confirmed by the experience of my friend Mr. John Thom, of Birkacre, near Chorley, one of the most skilful of the Lancashire printers. From some incidental notices of munjeet in Persoz and similar writers, and a few experiments which I made some years ago, I was led to suspect that the colouring matters in munjeet, though similar, are by no means identical with those of ordinary madder, and that probably the alizarine or purpurine of madder would be found to be replaced by some corresponding colouring principle. This hypothesis I have found to be essentially correct; for the colouring matter of munjeet, instead of consisting of a mixture of alizarine and purpurine, contains

no alizarine at all, but purpurine and a beautiful orange colouring matter crystallizing in golden scales, to which I purpose giving the name of "munjistine." Munjistine exists in munjeet in considerable quantity, and can therefore be easily obtained.

The colouring matter of munjeet may be extracted in various ways; that which I have found most suitable is as follows:—each pound of munjeet in fine powder is boiled for four or five hours with two pounds of sulphate of alumina and about sixteen of water. The whole of the colouring matter is not extracted by a single treatment with sulphate of alumina; the operation must be repeated therefore two or three times. The red liquid thus obtained is strained through cloth filters while still very hot, and the clear liquor acidulated with hydrochloric acid. It soon begins to deposit a bright red precipitate, the quantity of which increases on standing, which it should be allowed to do for about twelve hours. This precipitate is collected on cloth filters and washed with cold water till the greater portion of the acid is removed. It is then dried, reduced to fine powder, and digested in a suitable extracting apparatus with boiling bisulphide of carbon, which dissolves out the crystallizable colouring principles of the munjeet, and leaves a considerable quantity of dark-coloured resinous matter. The excess of the bisulphide of carbon having been removed by distillation, the bright red extract, consisting chiefly of a mixture of munjistine and purpurine, is treated repeatedly with moderate quantities of boiling water and filtered. The munjistine dissolves, forming a clear yellow liquid, while almost the whole of the purpurine remains on the filter. When this solution is acidulated with hydrochloric or sulphuric acid, the munjistine precipitates in large yellow flocks. These are collected on a filter and washed slightly with cold water. The precipitate is then dried by pressure, and dissolved in boiling spirit of wine slightly acidulated with hydrochloric acid to remove any adhering alumina. As the munjistine does not subside from cold alcoholic solutions, even when they are largely diluted with water, about three-fourths of the spirit are drawn off by distillation, when the munjistine is deposited in large yellow scales. By two or three crystallizations out of spirit in the way just described the munjistine is rendered perfectly pure.

I have likewise succeeded in extracting munjistine directly from munjeet by boiling it with water, filtering the solution, which has a dark brownish-red colour, and then acidulating with hydrochloric

acid. The precipitate which falls is collected on a filter, washed, dried, and treated with boiling spirit of wine, which leaves a large quantity of pectine undissolved. The munjistine which dissolves in the alcohol is obtained in a pure state by repeated crystallizations in the way already indicated. The first process which I have described is, however, by far the best. The colouring matter of munjeet can likewise be extracted with boiling solutions of alum; but I find sulphate of alumina greatly preferable, as the alum, by its tendency to crystallize, very much impedes the filtration of the liquids. I likewise attempted to employ Professor E. Kopp's process with sulphurous acid, which gives such excellent results with ordinary madder, but I found it wholly inapplicable to munjeet.

Munjistine, prepared by the processes described, when crystallized out of alcohol, forms golden-yellow plates of great brilliancy. It is but moderately soluble in cold, but dissolves pretty readily in boiling water, forming a bright yellow solution, from which it is deposited in flocks when the liquid cools. Saturated solutions almost gelatinize. It dissolves to some extent in cold, but more readily in boiling spirit of wine, and is not precipitated by the addition of water. It dissolves in carbonate of soda with a bright red colour. In ammonia it forms a red solution with a slight tinge of brown: caustic soda produces with it a rich crimson colour. Both its aqueous and alcoholic solutions, when boiled with alumina, form beautiful flakes of a bright orange colour, almost the whole of the munjistine being withdrawn from solution. These flakes are soluble in a large excess of caustic soda, with a fine crimson colour. Munjistine dyes cloth mordanted with alumina a bright orange. With iron mordant it yields a brownish-purple colour, and with Turkey-red mordant a pleasing deep orange. These colours are moderately permanent, and bear the application of bran and soap tolerably well. The munjistine sensibly modifies the colours produced by munjeet, giving the reds a shade of scarlet, as has been long observed.

Commercial nitric acid dissolves munjistine with a yellow colour, but does not appear to decompose it even on boiling. Fuming nitric acid (1·5) dissolves munjistine in the cold, and on application of heat decomposes it, no oxalic acid being produced. It readily dissolves in cold sulphuric acid with a bright orange colour; and the solution may be heated nearly to boiling without blackening or

giving off sulphurous acid; it is reprecipitated by water in yellow flocks apparently unaltered. When bromine water is added to a strong aqueous solution of munjistine, a pale-coloured flocculent precipitate is immediately produced; this, when collected on a filter, washed and dissolved in hot spirit, furnishes minute tufts of crystals, evidently a substitution product. I may remark, in passing, that when alizarine is treated with bromine water in a similar way, it also forms a substitution product crystallizing in needles. I am at present engaged in the examination of both these compounds.

When munjistine is strongly heated on platinum foil, it readily inflames and leaves no residue; when it is carefully heated in a tube, it fuses, and crystallizes again on cooling. It sublimes more readily than either purpurine or alizarine, forming golden scales which consist apparently of unaltered munjistine, as they give the characteristic rich crimson coloration with caustic alkalies. Baryta water produces a yellow precipitate with munjistine. Acetate of lead throws down a bright crimson precipitate, both in its aqueous and alcoholic solutions. I expect, from this and the bromine substitution compound, very shortly to ascertain the atomic weight of this body; in the mean time I submit the results of its ultimate analysis.

I. ·314 grm. of munjistine yielded ·732 grm. of carbonic acid and ·106 grm. of water.

II. ·228 grm. munjistine yielded ·535 grm. carbonic acid and ·0765 grm. water.

	I.	II.
C per cent.	63·6	64·0
H ,,	3·77	3·73
O ,,	32·63	32·27
	100·00	100·00

The munjistine operated upon in each case was prepared at different times; moreover No. 1 was burnt with oxide of copper, No. 2 with chromate of lead.

Munjistine in some of its properties bears considerable resemblance to Runge's madder-orange, the "rubiacine" of Dr. Schunck: it is, however, essentially different from rubiacine, both in several of its properties, such as its solubility in water and alcohol, &c., and in the amount of its carbon—rubiacine, according to Dr. Schunck's analysis,

containing 67·01 per cent. of that element, while munjistine contains only 64. The spectra afforded by solutions of the two substances, as may be seen from the following extract from a letter received from Professor Stokes, are decidedly different.

"The two substances are perfectly distinguished by the very different colour of their solution in carbonate of soda, when a small quantity only of substance is used. The solution of munjistine is red inclining to pinkish orange, that of rubiacine a claret-red. The tints are totally different, and indicate a different mode of absorption. Both present a single minimum in the spectrum; but while that of rubiacine extends from about D to F, that of munjistine extends from a good way beyond D to some way beyond F. The beginning and end of the band in each case is not very definite, and varies of course with the strength of the solution; but by comparing the substances with different strengths of solution, there can be no doubt of the radical difference in the position of the band of absorption. In this way it is easy to convince oneself that the difference of colour is not to be explained by the possible admixture of some small impurity present in one or other specimen. With caustic potash munjistine gives as nearly as possible the same colour as rubiacine, agreeing with the colour of rubiacine in carbonate of soda. There appears to be a slight difference in the spectrum of the munjistine and rubiacine solutions, but not enough to rely on; so that the substances are not to be distinguished by their solutions in *caustic* alkalies.

"A second perfectly valid distinction is, however, afforded by the different colour of the fluorescent light of the ethereal solutions. The solid substances themselves and their ethereal solutions are fluorescent to a considerable degree; but the tint of the fluorescent light of the ethereal solution of rubiacine is orange-yellow, while that of the ethereal solution of munjistine is yellow inclining to green. The examination in a pure spectrum shows that the difference is not due to the admixture of a small impurity, itself yielding a fluorescent solution; but the tints may be readily contrasted by daylight, almost without apparatus, by the method I have described in a paper 'On the existence of a second crystallizable fluorescent substance in the bark of the horse-chestnut' (Quart. Journal Chem. Soc. vol. ii. p. 20). I consider either of the two points of difference I

have mentioned sufficient by itself to establish the non-identity of munjistine and rubiacine" *.

The purpurine which I succeeded in extracting from munjeet and in purifying from munjistine in the way already described, formed beautiful dark crimson needles, having all the usual properties of that substance. When examined by Professor Stokes, they gave the very characteristic spectra of purpurine.

·3285 grm. of purpurine gave ·8005 grm. carbonic acid and ·1050 grm. water.

	Analysis.		
	Theory.	Found.	Debus (mean).
C........	66·67	66·46	66·40
H........	3·70	3·55	3·86
O........	29·63	29·99	29·74
	100·00	100·00	100·00

From the results above detailed there can therefore be no doubt that the colouring matter of munjeet, as already stated, consists of purpurine and munjistine.

I cannot conclude this preliminary notice without acknowledging the essential services I have received from Professor Stokes, who kindly submitted the different products obtained by me to optical examination. Though it is plain that a substance optically pure, that is, containing no impurities affecting the spectrum, may still be far from being chemically so, yet the spectroscope is extremely useful in indicating admixtures of kindred substances of very similar properties, having a great affinity for each other, and therefore not readily separable. I feel certain therefore that if Professor Stokes would draw up a short treatise embodying his extensive and accurate observations on the spectra of the colouring matters and similar substances, he would confer a great boon on the cultivators of organic chemistry.

Postscript.—Received July 18, 1863.

Since the preceding paper was communicated to the Royal Society I have been enabled to examine the action of nitric acid on munjis-

* I may mention that the rubiacine which Professor Stokes examined was prepared by Dr. Schunck himself.

tine much more fully. When munjistine is digested with moderately strong nitric acid, as already stated, copious fumes are given off, the munjistine gradually dissolving and forming a colourless solution. When this is evaporated to dryness on the water-bath, a white crystalline mass is obtained, consisting almost entirely of phthalic acid contaminated with a small quantity only of oxalic acid. The oxalic acid may be easily removed by washing the mass with a little cold water and then pressing between folds of bibulous paper, or by neutralizing the mixture of the two acids with lime and then treating with boiling water, which dissolves the phthalate of lime. The acid freed from oxalic acid by either of these methods presents all the usual reactions of phthalic acid. One of the most convenient ways of purifying it consists in subliming it repeatedly in a Mohr's apparatus, when the anhydrous acid is obtained in beautifully white iridescent four-sided prisms, frequently several inches in length. ·3745 grm. of the crystals of the anhydride, burnt with chromate of lead, gave ·891 grm. carbonic acid and ·095 grm. of water.

	Theory.	Expt.	Marignac.	Laurent.
C_{16}.... 96	64·86	64·89	64·88	64·70
H_4.... 4	2·70	2·81	2·71	2·38
O_6.... 48	32·44	32·30	32·41	32·92

From this result it is evident that the acid chiefly produced by the action of nitric acid upon munjistine is phthalic acid, which, as is well known, may also be procured from alizarine and purpurine. This reaction, therefore, indicates a very close relationship between these three substances, the only true colouring principles of madder with which we are at present acquainted.

VI. "Notes of Researches on the Poly-Ammonias.—No. XXIV. On Isomeric Diamines." By A. W. Hofmann, LL.D., F.R.S. Received May 26, 1863.

In a former paper* I have described phenylene-diamine, an aromatic diamine which is formed by the action of powerful reducing

* Proc. Roy. Soc. vol. xi. p. 518.